Triple isotope effects accompanying evaporation of water: new insights from laboratory experiments

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Stable isotopes of hydrogen and oxygen ($^2$H and $^{18}$O) are often used for quantification of water budgets of lakes and other surface water bodies, in particular for the assessment of underground components of those budgets [1]. Recent advances in laser spectroscopy enabled simultaneous analyses of $^2$H, $^{18}$O and $^{17}$O content in water, with measurement uncertainties comparable ($\delta^{18}$O) or surpassing ($\delta^2$H) those routinely achieved by off-line sample preparation methods combined with conventional IRMS technique [2]. This open up the doors for improving reliability of isotope-aided budgets of surface water bodies by adding third isotope tracer ($^{17}$O). This, however, requires adequate information on triple isotope effects accompanying evaporation of water, in particular the kinetic isotope effect related to evaporation of $^1$H$_2^{17}$O isotopologue.

Here we present the results of dedicated laboratory experiments aimed at quantification of triple isotope effects accompanying evaporation of water under fully developed diffusive sublayer [3]. Identical containers with predefined mass of water of known isotopic composition were placed in an isolated chamber with controlled atmosphere during the experiment (temperature, relative humidity). The chamber was flushed with synthetic air. At regular time intervals (approximately one week) containers were removed one by one from the chamber, the remaining mass of water in the removed container was determined gravimetrically, and stored for subsequent isotope analyses. The flow rate was adjusted at each step of the process to keep humidity inside the chamber constant. Evaporation continued until approximately half of the initial mass of water was removed from the containers. The experiment was repeated under different conditions inside the chamber (two different temperatures and three different values of relative humidity).

The results of the experiments were interpreted in the framework of Craig-Gordon model of evaporation [3]. It turned out that the assumption often used in the description of isotopic effects accompanying evaporation that liquid phase is isotopically homogeneous during the process, leads to conflicting results for three isotope systems in use. However, if surface enrichment of the liquid phase, different for each heavy isotopologue ($^1$H$_2^{16}$O, $^1$H$_2^{18}$O, $^1$H$_2^{17}$O) is included in the model, consistent results for all three isotopes can be achieved, with calculated kinetic fractionation factor for $^1$H$_2^{17}$O isotopologue equal 14.76 ± 0.48 ‰. This value agrees, within the quoted uncertainty, with the value of 14.60 ± 0.30 ‰ obtained by Barkan and Luz [4].

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References: